AD-750 403

NEGATIVE ION DETACHMENT

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SUMMARY TECHNICAL REPORT

(1 June 1971 - 30 June 1972)

CONTRACT N00014-71-C-0386

NEGATIVE ION DETACHMENT

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ARPA ORDER NO. 1479

PROJECT CODE 421

PRINCIPAL INVESTIGATOR:

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EFFECTIVE DATE OF CONTRACT: 1 June 1971

CONTRACT EXPIRATION DATE: 30 June 1973

AMOUNT OF CONTRACT: $108,913

RESULTS

We have measured several associative detachment rates of F^- negative ions by various gases. These reactions studied are listed below.

$$F^- + F \rightarrow F_2 + e - 1.9\ eV \quad (1)$$

$$F^- + O_2 \rightarrow O_2 + e - 2.8\ eV \quad (2)$$

$$F^- + O \rightarrow OF + e - 0.5\ eV \quad (3)$$

$$F^- + CF_2 \rightarrow CF_3 + e + 0.5\ eV \quad (4)$$

Measurements on Reactions (1) and (2) had been started under the previous contract and were finished during the first part of this contract. Figures (1) and (2) show our measured rate constants and our fits to the data. All the rate constants which we have measured to date (including the previous work) are listed in Table I.

Our major aim under this contract was to measure Reaction (3), i. e. associative detachment of F^- by atomic oxygen. The source of atomic oxygen in these measurements is ozone (O_3) which breaks up under the conditions of our shock tube into equal mole fractions of O and O_2 so that we see simultaneous detachment by both O and O_2. Thus, the rate of detachment by O_2 had to be measured (previous contract)

MEASURE COLLISIONAL DETACHMENT RATE OF F^- BY F

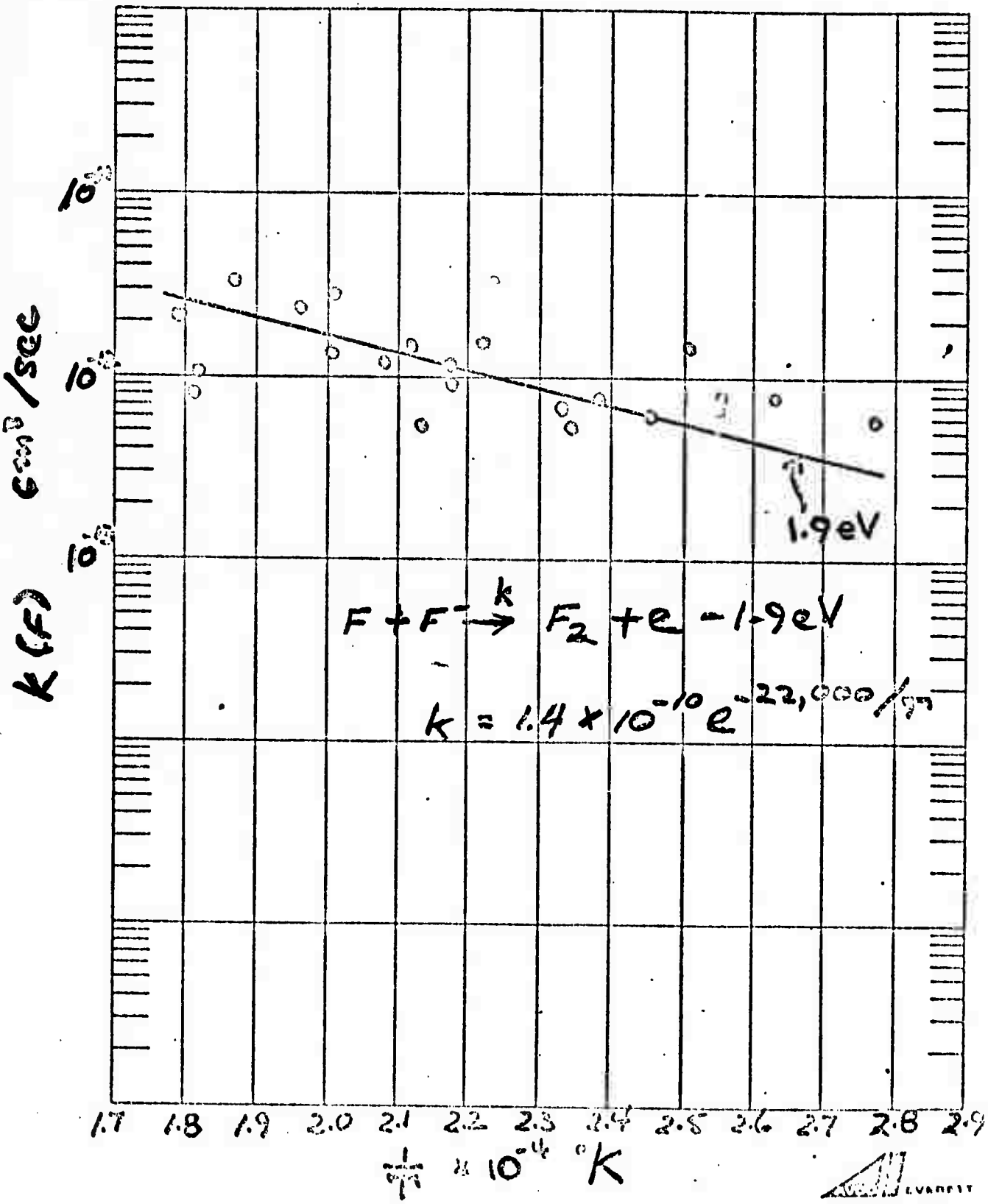

Fig 1

$F^- + O_2$

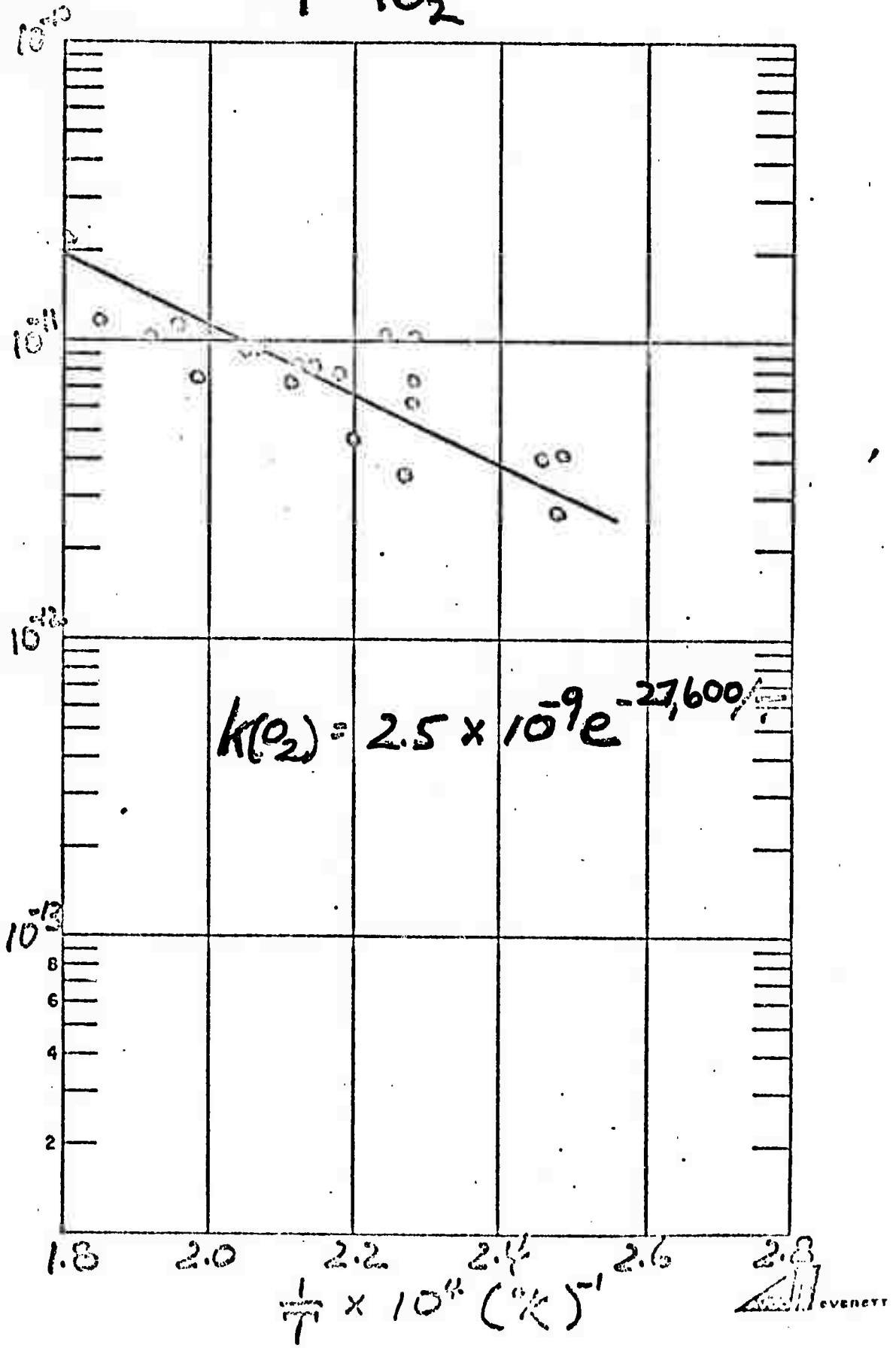
10^{-10}
10^{-11}
10^{-12}
10^{-13}
8
6
4
2
$k(O_2)$ (cm³/sec)
$k(O_2) = 2.5 \times 10^{-9} e^{-27,600/T}$
1.8
2.0
2.2
2.4
2.6
2.8
$\frac{1}{T} \times 10^4 (°K)^{-1}$
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Fig 2.

TABLE I

RATE CONSTANTS

REACTION	k (CM^3/SEC)
$F^- + Ar \rightarrow F + e + Ar$	$1.2 \times 10^{-11}\ e^{-40,000/T}$
$F^- + Cs^+ \rightarrow F + e + Cs^+$	$2.8 \times 10^{-9}\ e^{-40,000/T}$
$F^- + N_2 \rightarrow F + e + N_2$	$6.0 \times 10^{-11}\ e^{-40,000/T}$
$F^- + CO \rightarrow F + e + CO$	$1.7 \times 10^{-10}\ e^{-40,000/T}$
$F^- + H_2 \rightarrow HF + H^-$	$2.8 \times 10^{-11}\ e^{-9,400/T}$
$F^- + F \rightarrow F_2 + e$	$1.4 \times 10^{-10}\ e^{-22,000/T}$
$F^- + O_2 \rightarrow O_2F + e$	$2.5 \times 10^{-9}\ e^{-27,600/T}$
$F^- + O \rightarrow OF + e$	$2.0 \times 10^{-10}\ e^{-14,600/T}$
$F^- + CF_2 \rightarrow CF_3 + e$	$\sim 10^{-12}$

and subtracted from these data. Our measured rates of detachment of F^- by O and O_2 are given in Fig. 3. Note that at the high temperature end ($T \sim 5000^oK$) the O and O_2 detachment rates become comparable but in the region of interest for boundary layer conditions, i. e. $T \sim 2800^oK$, the atomic oxygen detachment rate dominates. We will discuss the significance of this below.

As I had mentioned in one of the quarterly management reports, there were two milestone experiments which we had to perform initially in order to insure that we would be able to, in fact, use ozone in our system. First, we had to insure that our shock tube could hold ozone for reasonable periods of time without significant decomposition to O_2. In order to assure this, the tube had to be passivated. Passivation is a process in which the stainless steel walls of the shock tube are allowed to be oxidized by the highly active ozone until sufficient oxides build up on the surface making it non-reactive to ozone.

In order to show this passivation, we did the following experiment: A one meter cell for measuring ozone concentrations was attached to our shock tube. The one meter cell had a stainless steel seal which was not yet exposed to ozone and therefore not passivated. There is a valve separating the shock tube from the cell. The shock tube was filled with a mixture of ozone and argon gas. Periodically (about once an hour) the one meter cell was filled with the ozone mixture from the shock tube and the valve then closed. We then monitored the ozone in the one meter cell. The first measurement, immediately after the cell is filled, tells us essentially what the

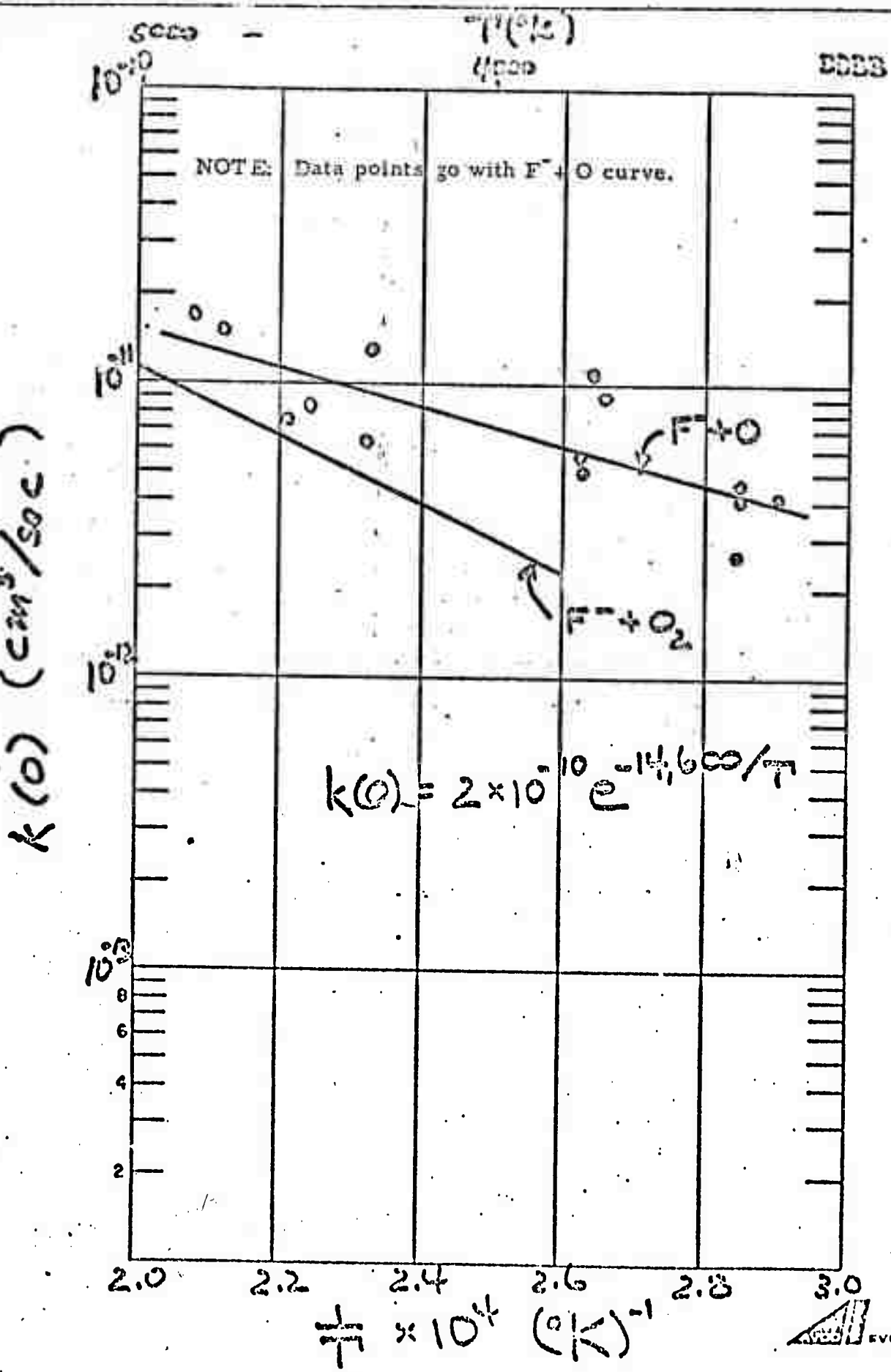
NOTE: Data points go with F⁻ + O curve.
F⁻ + O
F⁻ + O₂
k(0) = 2×10⁻¹⁰ e^(-14,600/T)
k(0) (cm³/sec)
10⁻¹⁰
10⁻¹¹
10⁻¹²
10⁻¹³
8
6
4
2
2.0
2.2
2.4
2.6
2.8
3.0
1/T ×10⁴ (°K)⁻¹
EVERETT

Fig 3

concentration of ozone is in the shock tube, since not much decay has yet occurred in the cell. The ozone density measurements after this, however, gives us the rate of ozone decay in the cell. The cell is pumped out after this decay is observed, and after one hour the process is repeated. Thus, the first measured point in each case gives us the decay rate of ozone in the shock rube. Figure 4 shows data obtained in the above manner after passivating the shock tube. Note that during the course of these measurements we see that the decay rate in the one meter cell is slowing, i.e. the cell is being passivated.

The second milestone experiment was to measure the effect of particulates (.07μ CsF particles in our case) on ozone decomposition. We observed that over the time scale of our experiment, i.e. ~ 60 seconds, no significant ozone decomposition was seen. Measurements of this type are, of course, of great significance for upper atmospheric physics. To my knowledge, these are the first laboratory measurements of the survival of ozone in gas containing a known quantity of particulates.

With the knowledge that ozone would not significantly decay when mixed with CsF particles in our passivated shock tube, we were able to proceed with our measurements. These results are summarized in Fig. 3.

Finally, we have made some measurements of F^- detachment by CF_2. The CF_2 is produced by the decomposition of C_2F_4 (a very rapid process) at the shock front. We have not fully analyzed this data yet but it does give a rate of roughly 10^{-12} cm^3/sec. This rate should not have a large temperature dependence since the reaction $CF_2 + F^- \rightarrow CF_3 + e$ is exothermic.

PASSIVATION OF METER CELL

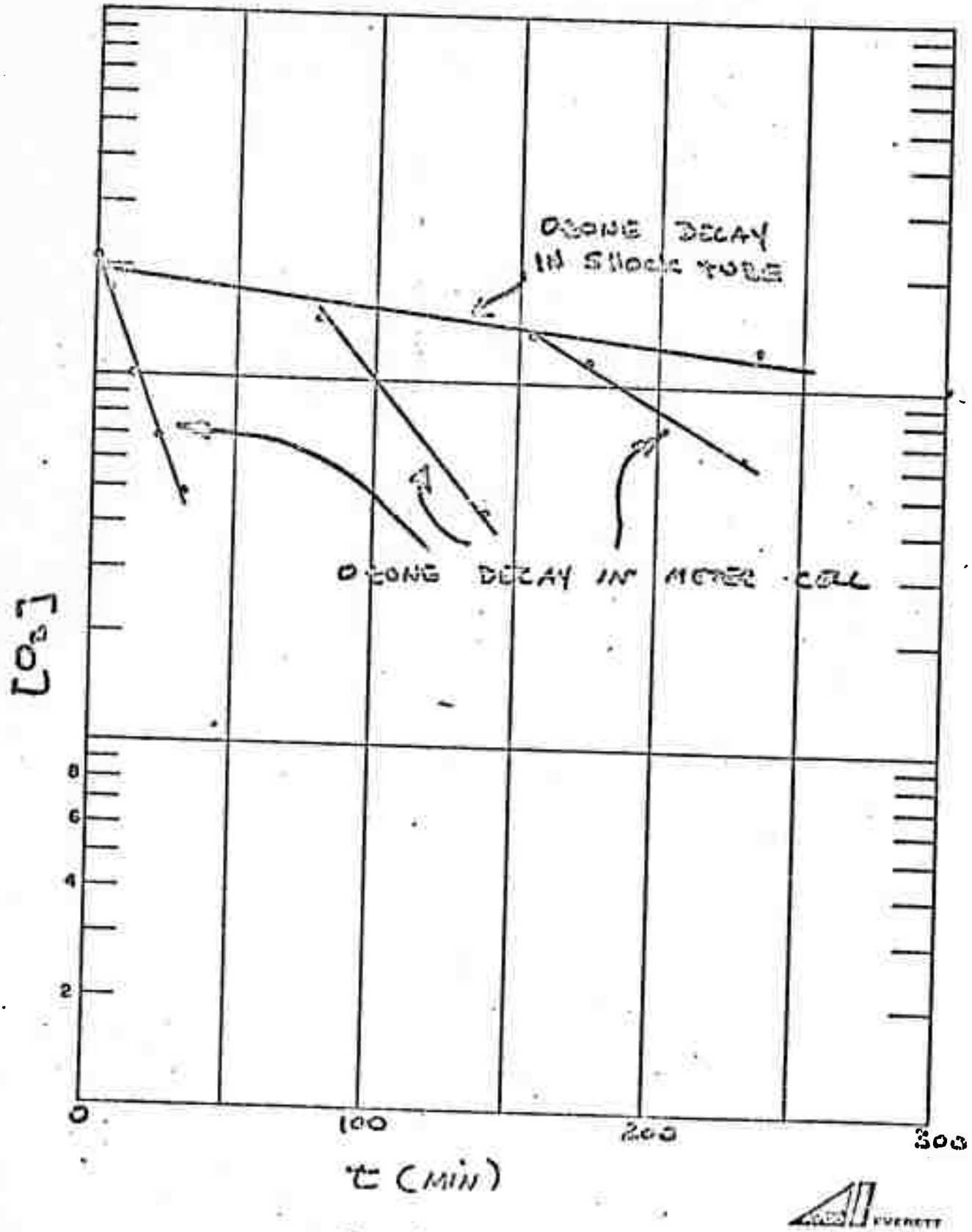

Fig 4

SIGNIFICANCE OF MEASUREMENTS

The original purpose of this program was to supply F^- collisional detachment rates for the 14 species limited-partial-equilibrium model developed at AERL for the Teflon boundary layer. A major assumption of this model was that all the F^- was detached in the boundary layer, i. e. all electrons were free. However, there were no kinetics data to support this assumption. As we measured our detachment rates of F^-, it became clear that none of our measurements for species like N_2, O_2, etc., present in the boundary layer gave rates fast enough to detach F^-. Thus, the validity of one of the main assumptions of the 14 species limited partial equilibrium model became questionable.

Figure 5 gives the minimum detachment rate (solid lines) necessary for different species at various altitudes to produce detachment by F^- in boundary layer flow times. The dashed lines are our measured detachment rates. It is clear that our measured detachment rates for N_2, CO, F, and O_2 detachment are too low. We had suggested,therefore, that because of its possibly low activation energy, the rate of detachment of F^- by atomic oxygen might be fast enough to cause F^- detachment in the boundary layer. The measurements obtained for atomic O show that F^- detachment by atomic oxygen is fast enough to give complete detachment in the boundary layer of a Teflon vehicle and tends to support the AERL model.

If it had turned out that detachment by O was not fast enough to give full F^- detachment in the boundary layer, then the 14 species model would have had to be significantly revised and possible detachment

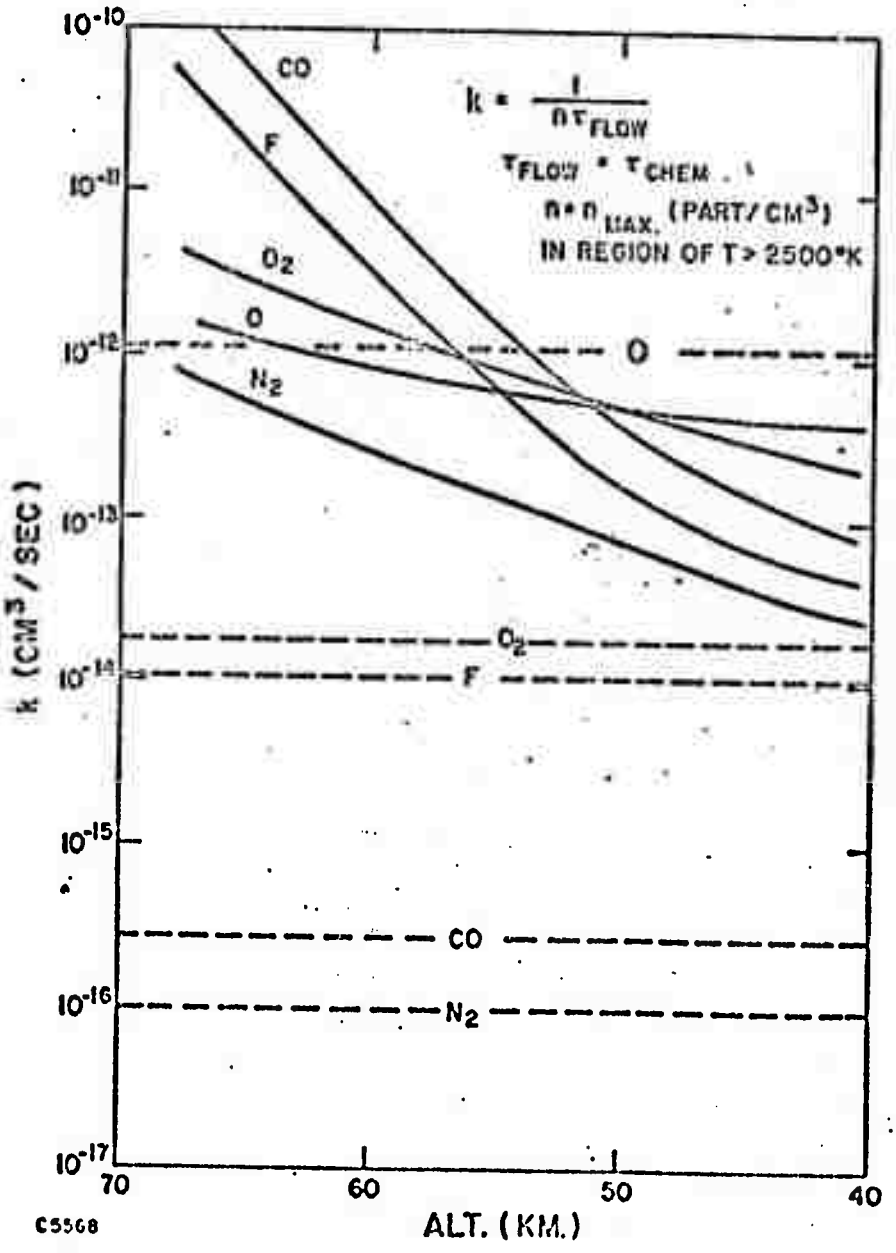

Fig. 5 Minimum Rate Constants for Electron Detachment. Solid lines give minimum values of the rate constant necessary for complete detachment of F^- in the boundary layer of a Teflon ablating vehicle at various altitudes. The density, n, used is the maximum value of density, $n_{max.}$, in the region of the boundary layer above 2500°K as given by the AERL model in which 14 species are in equilibrium. The dashed curves are our measured values of rate constants. Complete detachment will occur below the intersection of a dashed and solid curve of the same species.

by CF_2 would have had to be considered. In that case detachment by CF_2 would have been quite important, and we had planned to measure this rate as part of this program. In any case we have measured the CF_2 detachment rate, although the significance of this rate to the overall program is now of lesser importance.

PUBLICATIONS

1. A. Mandl, J. Chem. Phys. 55, 2918 (1971). Thermal dissociation rate of CsF.

2. A. Mandl, J. Chem. Phys. 55, 2922 (1971). Collisional detachment rate of CsF.

3. R. E. Center and A. Mandl, J. Chem. Phys., to be published 15 November, 1972. Electron impact ionization cross section of F_2 and estimate of polarizability of F_2.

4. A. Mandl, J. Chem. Phys. to be published 15 December 1972. Collisional detachment rate of F^- by CO and H_2.

TALKS

A. Mandl, Bulletin of the American Physical Society, 17, 621 (1972). Collisional detachment rate of F^- by CO and H_2.